Test Material: Dicamba

MRID: 49888503

Title: Field Volatility of Dicamba Formulation MON 119096 Following a Post-Emerge Application Under Field Conditions in Texas

EPA PC Code: 128931

OCSPP Guideline: 835.8100

For CDM Smith

Primary Reviewer: Richard Lester   **Signature:**

Date: 7/28/16

Secondary Reviewer: Dan Hunt   **Signature:**

Date: 7/28/16

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Date: 7/28/16

Field Volatility of Dicamba

Report:	MRID 49888503. Jacobson, B., Urbanczyk-Wochniak, E., Mueth, M.G., Riter, L.S., Sall, E.D., Honegger, J., South, S., Carver, L. 2016. Field Volatility of Dicamba Formulation MON 119096 Following a Post-Emerge Application Under Field Conditions in Texas. Unpublished study performed by Waterborne Environmental, Inc., Leesburg, Virginia; Monsanto Company, St. Louis, Missouri; and Agvise Laboratories, Northwood, North Dakota. Study sponsored by Monsanto Company, St. Louis, Missouri. Monsanto Study No.: WBE-2015-0311; Waterborne Study No.: 666.14. Study initiation June 2, 2015, and completion March 30, 2016 (p. 7).
Document No.:	MRID 49888503
Guideline:	OCSPP 835.8100
Statements:	This study was conducted according to the USEPA FIFRA Good Laboratory Practice (GLP) Standards (40 CFR Part 160), with the following exceptions:

Field Phase:
1) Test site information such as estimation of slope, elevation, and GPS coordinates.
2) Study weather data.
3) Pesticide and crop histories for the test plots.
4) Soil information provided by the USDA Natural Resources Conservation Service (NRCS)
5) Test plot preparation prior to application.
6) Weight of the 1lb subsamples for soil characterization analysis.

Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).

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Classification:	This study is supplemental. The decline of the test material was not clearly established. The minimum fetch required for use of the aerodynamic method was not satisfied for all samplers. The initial air monitoring period did not start at the beginning of the application period, but instead started immediately following the application period. An independent laboratory method validation was not conducted.
PC Code:	128931
Reviewer:	William P. Eckel, Ph.D. **Signature:** _William P. Eckel_
	Senior Science Advisor, ERB6 **Date:** 10/11/2016

Executive Summary

Field volatilization of dicamba, formulation MON 119096, a dicamba diglycolamine salt formulation containing 350 g dicamba acid equivalent (a.e.)/L, was examined from a cropped plot at one site in Fort Bend County, Texas. The site where the study was conducted was near Kendleton, TX. The experiment at this site (Site 1/Plot 1) was conducted for approximately three

days. The nominal application rate in the plot was 0.5 lb. a.e./A. This plot was approximately 1000 ft generally upwind from a plot for another study conducted on the same days.

Under field conditions at Site 1/Plot 1, based on calculations using the Integrated Horizontal Flux method, dicamba in the MON 119096 formulation had a peak volatile flux rate of 0.000277 $\mu g/m^2 \cdot s$ accounting for 0.023% of the applied observed 17.3 to 30.3 hours post-application. By the end of the study, a total of 0.06 % of the applied dicamba volatilized and was lost from the field after application. Other secondary peak volatile flux rates of 0.000197 $\mu g/m^2 \cdot s$ and 0.000226 $\mu g/m^2 \cdot s$ occurred at 0 to 6.7 and 41.3 to 54.3 hours post-application, respectively. Higher flux rates were observed during the first day after application and during the daytime on Days 2 and 3.

Under field conditions at Site 1/Plot 1 based on calculations using the Aerodynamic Flux method, dicamba in the MON 119096 formulation had a peak volatile flux rate of 0.000218 $\mu g/m^2 \cdot s$ accounting for 0.018% of the applied observed 17.3 to 30.3 hours post-application. By the end of the study, a total of 0.041% of the applied dicamba volatilized and was lost from the field after application. Other secondary peak volatile flux rates of 0.000074 $\mu g/m^2 \cdot s$ and 0.000188 $\mu g/m^2 \cdot s$ occurred at 0 to 6.7 and 41.3 to 54.3 hours post-application, respectively. Higher flux rates were observed during the first day after application and during the daytime sampling on Days 2 and 3.

Figure 1. Dicamba Flux Rates
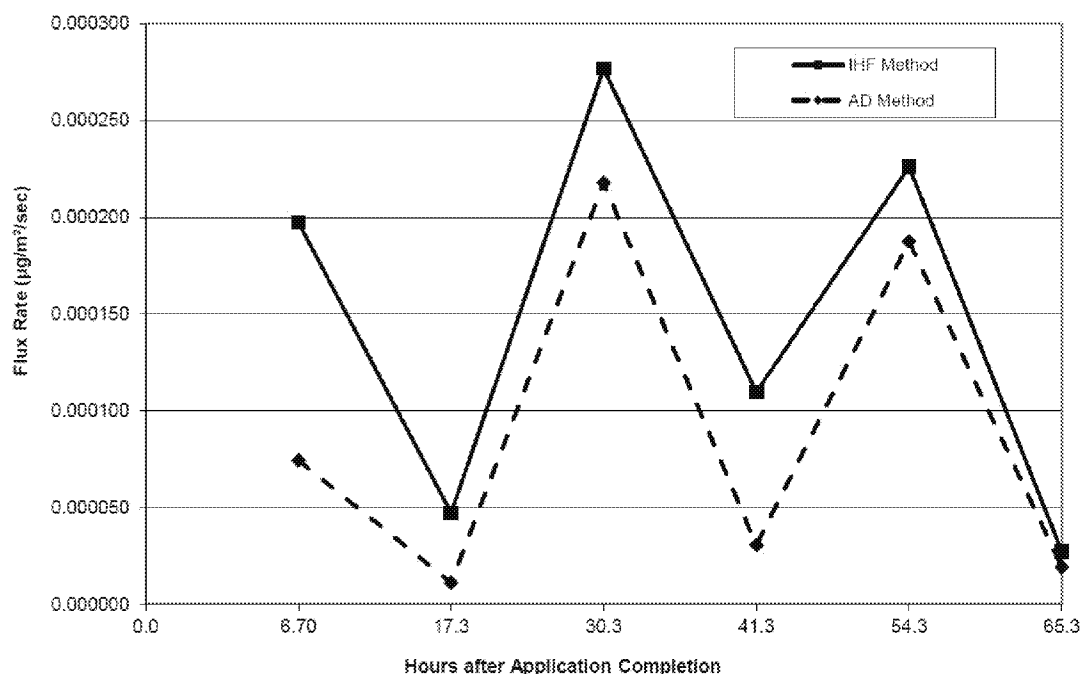
I. Materials and Methods

A. Materials

1. Test Material   Product Name: MON 119096 (p. 17)
Formulation Type: Liquid
CAS #: 104040-79-1 (dicamba
diglycolamine salt)
Storage stability: Stability of the active
ingredient dicamba in the test
substance MON 119096 has previously
been demonstrated for 14 days at 55°C and for a related
formulation one year under heated warehouse conditions
(Appendix 5, p. 88).
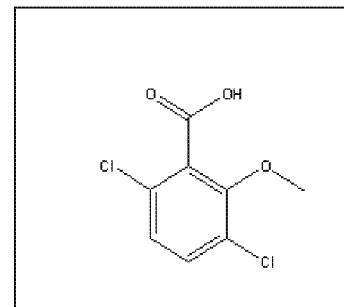
2. Storage Conditions

The test substance was shipped under ambient conditions by Monsanto Company on May 27,
2015 and received by AgGro Innovations, LLC (AgGro) in Cypress, Texas on June 2, 2015 (p.
17). Upon receipt, the test substance was stored in a pesticide storage area at ambient
temperatures ranging from approximately 71 to 75 °F prior to the application. On June 8, 2015
the test substance was transported to the test site at ambient temperatures ranging from
approximately 73 to 96 °F.

B. Study Design

1. Site Description

The test site was located near Kendleton, TX in Fort Bend County (pp. 17-18). A 9.6 acre (3.9
ha) plot was located in a larger field of cotton, planted with a variety of Bollgard II®
XtendFlex™ Cotton containing the dicamba tolerance trait, at the 6-8 leaf growth stage. The
plot dimensions were 648 ft x 648 ft (197.5 m x 197.5 m). The soil type of the plot was
classified as a Lake Charles clay, a very deep, moderately well drained, very slowly permeable
soil on broad coastal prairies that formed in clayey sediments. The taxonomic class of the Lake
Charles series is – fine, smectic, hyperthermic Typic Hapluderts (Order – Vertisols, Suborder –
Uderts). The crops on this site for the previous three years were cotton (2012), cotton (2013),
and grain sorghum (2014; Table 2, p. 36). No herbicides containing dicamba had been used on
the site for the last three years, although a number of other cotton and grain sorghum herbicides
had been used. This plot was located approximately 1000 feet upwind from a plot being used for
another study.[1] The elevation of the site was approximately 105 feet above sea level with the
slope in the test area estimated to be approximately 1%. The surrounding area was agricultural
fields.

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[1] Information regarding the distance from plots used for other studies is from the registrant-prepared study profile
for MRID 49888503.

2. Application Details

Application rate(s):   The target application rate was 0.5 lb a.e./A (0.561 kg/ha) (p. 19). Based on application monitoring samples in the treated area, the measured application rate ($\pm$RSD) was $104 \pm 9\%$ of the target application rate (p. 27; Table 7, p. 41). All nozzles were calibrated and pass times were within 2.5% of the target pass time (pp. 27-28).

Irrigation and Water Seal(s): No irrigation water was used.

Tarp Applications: Tarps were not used.

Application Equipment: A self-propelled sprayer (John Deere 4730) was used for the broadcast application of the dicamba formulation MON 119096 to the treated plot (p. 19). The spray boom was fitted with 72 Turbo Teejet Induction (TTI 11004) nozzles and 50 mesh screens. The nozzles were spaced 18 inches apart, providing a 108-foot swath width. The boom height was set approximately 14-18 inches above the crop canopy. The sprayer was equipped with an 800 gallon tank, and a centrifugal pump (hydraulically driven) was used to pressurize the system and provide agitation (recirculation).

Equipment Calibration
Procedures: The sprayer output prior to application was calibrated using water, and the spray from each nozzle was collected for 30 seconds in three separate runs (p. 19). The boom pressure was set at approximately 25 psi for the calibration trial and test substance application. The calibrated sprayer output for the application was calculated to be 15.35 GPA (Table 4, p. 38). The target sprayer speed was 10.60 feet/sec or 7.23 mph.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**. The adjuvant Induce® (0.25% v/v) was added to the spray mixture (p. 19).

Table 1. Summary of application methods and rates for MON 119096

Field	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied (lbs)	Area Treated (acres)	Target Application Rate (lb ae/acre)	Reported Application Rate (lb ae/acre)
1	Broadcast Spray	6/8/2015 13:15	5.05[1]	9.64	0.50	0.53[1]* 0.52[1]**

Data obtained from pp. 19, 27-28; and Table 5, p. 39.
[1] Not reported in the MRID. Data obtained from the registrant-prepared study profile for MRID 49888503.
*Based on sum of pass times, total sprayer output per second, and amount of formulation in the total spray volume. Note that more formulation was added to the spray tank than needed based on use of an incorrect nozzle spacing in the calculation.
**Based on analysis of deposition in the spray area (104% of the target 0.5 lb ae/acre application rate; p. 27).

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

Table 2. Summary of MON 119096 application and monitoring schedule

Field/Plot	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
Field 1 /Plot 1	9.6	06/08/15 between 13:15 – 13:40	06/08/15 between 13:40 – 20:22	Not Applicable	Not Applicable

Data obtained from p. 18 and Tables 5-6, pp. 39-40.

3. Soil Properties

Soil properties measured before the study are provided in **Table 3**.

Table 3. Summary of soil properties for fields/plots

Field	Sampling Depth	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm³)	Soil Composition
1	0-6 inches	Clay	Lake Charles Clay	Fine, smectic, hyperthermic Typic Hapluderts (Order – Vertisols, Suborder – Uderts)	1.14	% Organic Matter = 1.5% % Sand = 26% % Silt = 23% % Clay = 51%

Data obtained from p. 18 and Table 3, p. 37.

Figure 2 presents a plot of the soil surface temperature measured 1 mm below the soil surface during the time of the study (Appendix 1, pp. 58-62). Figure 3 presents a plot of the volumetric water content (VWC) as fraction of total soil volume at a depth of 2 inches (Appendix 1, pp. 58-62). Note that the VWC measurement is a relative measurement since the probe was not calibrated to the specific soil and the test site.
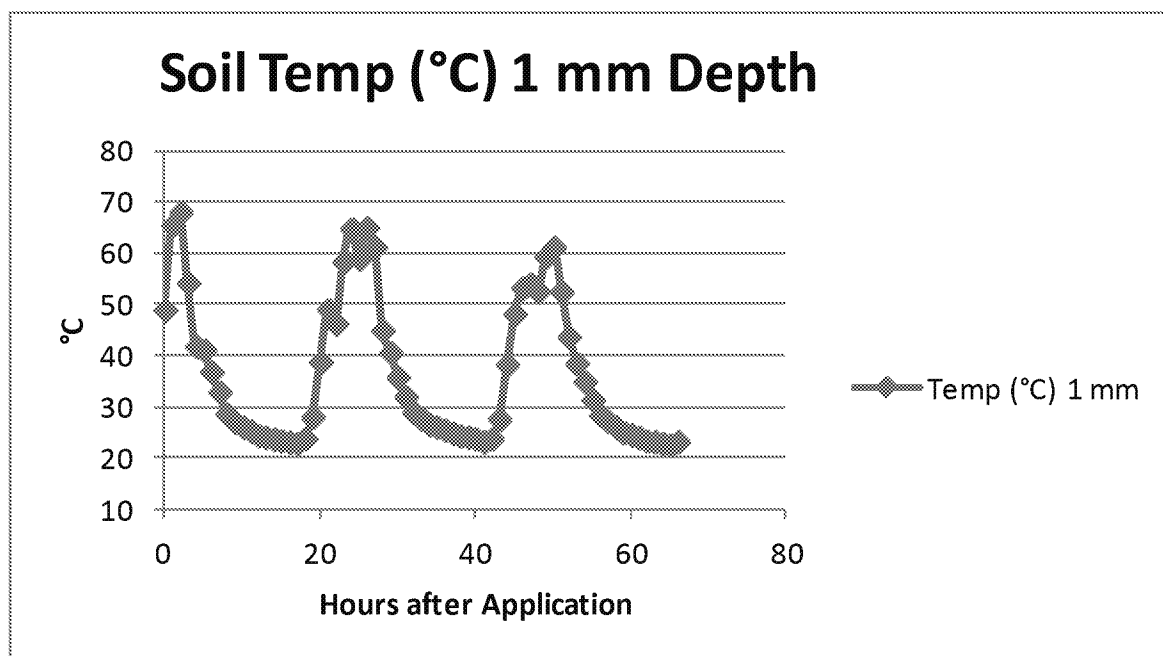
Figure 2. Soil Temperature at the Soil Surface (1mm Depth) after Application

Figure reported by the registrant in the registrant-prepared study profile for MRID 49888503.
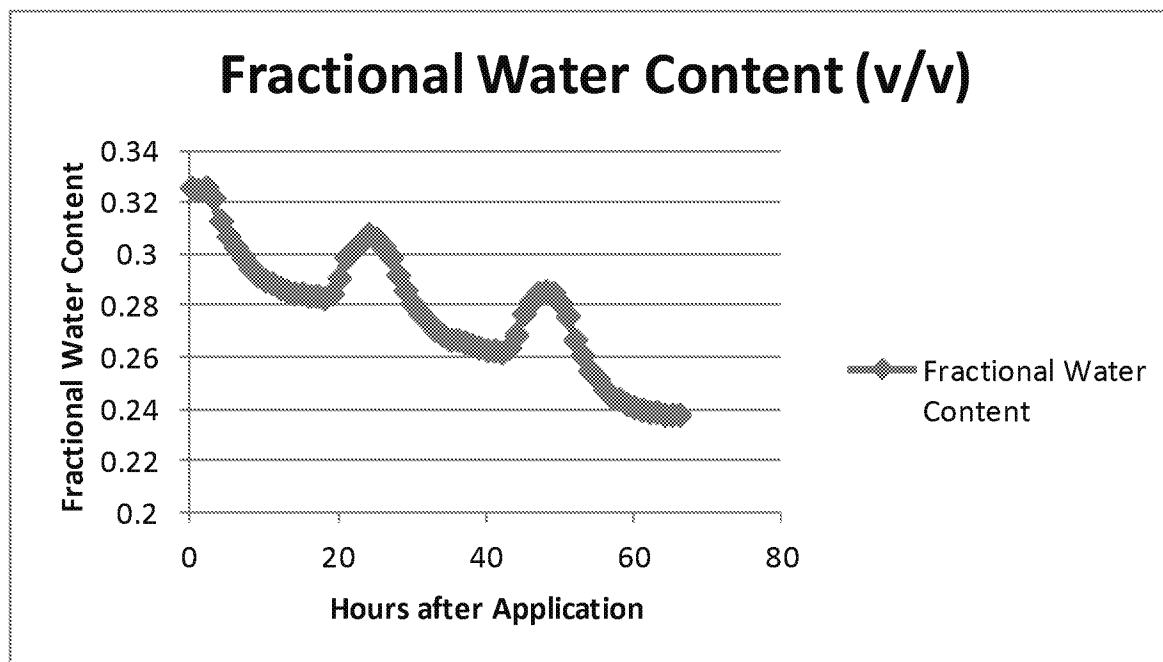

Figure 3. Soil Volumetric Water Content after Application

Figure reported by the registrant in the registrant-prepared study profile for MRID 49888503.

4. Meteorological Sampling

Air temperature, precipitation, relative humidity, solar radiation, wind speed, wind direction, soil temperature (1 mm and 2 and 6 inches deep) and reference evapotranspiration, were recorded at the test site using an on-site weather station (p. 18). A summary of hourly and daily climatological data including air temperature (max/min/avg), relative humidity (max/min/avg), ETo, wind speed (max/min/avg), average wind direction, solar radiation, soil temperature (max/min/avg), volumetric water content, and precipitation for the duration of the field volatility sampling is presented in Appendix 1 (pp. 51-62) of the report.

One meteorological station was established near the plot so that a good representation of the wind pattern of the test plot was achieved (Figure 3, p. 47). The station monitored air temperature (using air temperature sensors and radiation shields), and wind speed and wind direction (using sonic anemometers) located at approximately 0.33, 0.55, 0.90 and 1.5 m above the crop canopy (p. 21). Each parameter was measured every second, and the data were summarized every minute and every hour. The hourly wind speed and direction data for each monitoring height is summarized in Appendix 2 (pp. 63-68) of the report. The hourly air temperature data for each monitoring height is summarized in Appendix 3 (pp. 69-74) of the report. The temperature, wind speed, and wind direction at each sampling height summarized on a per minute basis is provided in the Raw Met Data worksheet in the Excel spreadsheets embedded in Attachment 2 of this document.

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in Table 4. The location of the meteorological equipment for the plot is shown in Attachment 3.

Table 4. Summary of meteorological parameters measured in the field

Field	Minimum Fetch* (m)	Parameter	Monitoring heights (m)	Averaging Period
1	107.8[1] (101.2)**	Wind speed/Wind direction	Height 0.33, Height 0.55, Height 0.90, Height 1.5	1 minute
		Ambient air temperature	Height 0.33, Height 0.55, Height 0.90, Height 1.5	1 minute
		Precipitation	Not reported	1 hour
		Evapotranspiration	Not reported	1 hour
		Relative humidity	Not reported	1 hour
		Solar radiation	Not reported	1 hour
		Soil temperature	Depth 1 mm, Depth 2 in, Depth 6 in	1 hour
		Soil moisture	Depth 1 mm, Depth 2 in, Depth 6 in	1 hour

Data obtained from pp. 18, 21; and Appendices 1-3, 7 (pp. 51-74, 274-275) of the study report.
[1] Not reported in the MRID. Data obtained from the registrant-prepared study profile for MRID 49888503.
* Value indicated is the minimum average fetch for a sampling period. Values on a per minute basis are calculated in the spreadsheets provided in Attachment 2.
**Value in parenthesis is from registrant submitted report MRID 49888503. In this report mean fetch for a sampling period is calculated using the resultant wind direction over the sampling period rather than calculating a fetch value for each minute during the sampling period and then taking the mean of those values.

5. Air Sampling

The on-field air profile monitoring station in the plot consisted of air sampling pumps mounted on a sampling mast located at the approximate center of the plot (pp. 20-21). Five sample locations (heights) were established on the sample mast at approximately 0.15, 0.33, 0.55, 0.90 and 1.5 m above the plant canopy. All air samples for a specific time increment were used for the regression analysis for that increment unless samples were disqualified by breakage or other defined cause. For each sampling time increment, a mass rate of chemical transfer per unit surface area (flux rate) was calculated. Two pre-application (PA) samples were collected at the 0.15 m height above the plant canopy near the air monitoring location (center of plot) in the treated plot on June 7, 2015 prior to the start of the application on the following day (Table 6, p. 40). Samples were collected from 8:43 until 15:40 on June 7.

6. Sample Handling and Storage Stability

Upon collection, the air sampling tubes were immediately placed in an ice chest with ice packs until they were transported to Paragon Research's mobile freezer located in Rosenberg, TX, approximately 16 miles from the test site (p. 22). Transit stability samples were prepared/spiked by Monsanto Company, and then shipped frozen to the field site then stored and shipped in the same manner as the actual field samples (p. 22). A set of air sampling tubes to be exposed in the field were prepared/spiked by Monsanto Company, and then shipped frozen to the field site (p. 22). At the field site, these samples were removed from frozen storage, allowed to reach ambient temperature then exposed to an air flow and placed in frozen storage along with the other field samples.

All samples were later shipped overnight via Federal Express in insulated containers with dry ice to Monsanto Company for analysis (p. 23). The samples were received frozen and were maintained frozen except when a sample was being prepared for extraction. Samples were then stored in a continuously monitored freezer set at approximately -20 °C until analysis (p. 23). All PUF samples in this study were extracted and analyzed within a period of less than 17 days after collection (Appendix 5, p. 89).

Stability of dicamba on PUF sample collectors has been demonstrated in a concurrent stability study (Appendix 5, p. 89; Appendix 6, p. 158). Samples were prepared by fortifying polyurethane foam (PUF) air sampling traps separately with dicamba at a concentration of 0.003 µg/PUF. Samples were removed from frozen storage and analyzed at intervals of 0, 7, 15, 55 and 78 days. The estimated degradation of dicamba was calculated using a statistical regression model. The statistical analysis of the change in measured concentration over time showed no statistically significant change in dicamba over the course of 78 days. Dicamba is therefore considered stable on PUF sample collectors under frozen storage conditions for at least a period of 78 days.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Dicamba was monitored using glass vapor collection tubes containing polyurethane foam (PUF) sorbent (SKC Inc. Catalog No. 226-92)

and SKC® (Model Number 224-52) personal air sampling pumps (p. 22). The vapor collection tubes were attached to a pump using Tygon® tubing. The flow for each sample was calibrated for each sample period using a Bios International model DCL-M, DC-L12K, DC-L5K flowmeter. The flow was set to approximately 3 L per minute.

- Extraction method: The PUF samples were transferred from the air sampling glass tube to a 50 mL conical tube and extracted by shaking for 30 minutes (1200 cycles per minute) using methanol containing stable-labeled internal standard (p. 24; Appendix 5, pp. 116-117; Appendix 6, p. 162). An aliquot of the supernatant was filtered, evaporated, reconstituted in 25% methanol in water and then dicamba was quantitated using LC-MS/MS with electrospray ionization in negative ion mode (Appendix 5, pp. 119-120).

- Method validation (Including LOD and LOQ): Method ME-1902-01 was validated by assaying 9 replicates each of samples fortified at 0.3 (LOQ), 3 and 60 ng/PUF (p. 24; Appendix 5, pp. 125-126). Capability of dilution was demonstrated using 3 replicate samples fortified at 600 ng/PUF. Validation assessments demonstrated accuracy within 70-120% and precision ≤20% RSD at all fortification levels tested. The specificity of the method was demonstrated through the analysis of control matrices. The limit of quantitation (LOQ) of dicamba was 0.3 ng/PUF determined during method development (Appendix 5, p. 108). The LOD was determined to be 0.065 ng/PUF through statistical determinations on validation data (Appendix 5, pp. 87, 90). Additional method validation performed on Method ME-1902 (same methodology as Method ME-1902-01; Appendix 5, p. 107) also showed acceptable mean recoveries (mean recovery between 70-120% and RSD ≤20%) at fortification levels of 0.30, 3.0, 60, and 600 ng/PUF (Appendix 5, Table 2, p. 95).

- Instrument performance: Calibration curves were linear with 1/x weighting (p. 90). The working range of the method was from 0.3 to 75 ng/PUF. Extension of the upper range of the method to 750 ng/PUF can be achieved using lower injection volumes, therefore overall the method covered sample concentrations from 0.3 to 750 ng/PUF.

8. Quality Control for Air Sampling

Lab Recovery: Most laboratory spike recoveries are within the acceptable range of 90-110% following fortification at 0.3, 3, 60, and 600 ng/PUF (p. 29; Appendix 5, p. 133); however, seven of 24 recoveries were outside the acceptable range. Recoveries outside the acceptable range included three of six laboratory spike samples with percent recoveries of 81.0, 84.0, and 88.7 at the fortification level of 0.3 ng/PUF and four of six laboratory spike samples with percent recoveries of 82.0, 110.8, 118.5, and 118.5 at the fortification level of 600 ng/PUF.

Field blanks: There was no dicamba measured in the samples collected before application (Table 3, p. 96).

Field Recovery: Mean recovery of dicamba from field spikes fortified at 3.0, 30.0 and 600 ng/PUF, and following either a 6- or 12-hour weathering period, ranged from 96.5 to 107% (overall recoveries of 90.5 to 110%; pp. 22-23, 28-29;

Appendix 6, Table 2, pp. 169-170); recoveries were similar across the
fortification ranges and weathering conditions. The length of storage was
not reported.

Travel Recovery: Mean recoveries of dicamba from transit stability samples fortified at 3.0
and 30.0 ng/PUF were 103% (range from 100 to 106%) and 100% (range
from 98.7 to 102%), respectively (Appendix 6, Table 3, p. 171). Transit
samples were stored for 17 days prior to extraction, and were stored in
the same manner as the test samples (p. 22).

Breakthrough: Samples that were fortified at 600 ng/PUF and exposed in the field for 12
hours had an average recovery of 96.5%. Samples fortified at 30 ng/PUF
and exposed for 12 hours had an average recovery of 98.8%. The highest
dicamba amount measured on a PUF (37.8 ng) was less than 7% of the
highest fortification (600 ng) indicating that dicamba loss due to
breakthrough did not occur at the dicamba air concentrations present in
this study (Appendix 4, pp. 76-78; Appendix 6, Table 2, pp. 169-170).

9. Application Verification

To verify the application of the test substance, ten application monitoring devices, pre-labeled
pans each containing five Whatman #3 filter papers (12.5 cm in diameter; total area of 614 cm^2)
were placed at random locations representative of the plot area (p. 20). As soon as possible
after application the five filter papers in each pan were placed into a pre-labeled 500 mL wide-
mouth, HDPE amber bottle, and each bottle was sealed and stored in an insulated cooler with ice
packs while in the field.

Recoveries achieved on extraction and analysis of application monitoring devices were in the
range of 95 to 127%, with a mean (±RSD) recovery of 104 ± 9% (n=10) (p. 27; Table 7, p. 41).
Recoveries achieved on extraction and analysis of laboratory fortification of application
monitoring filter papers ranged from 102 to 104% (p. 29).

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

For estimation of flux after application in this study, both the Aerodynamic Method and the
Integrated Horizontal Flux Method were used.

Aerodynamic Method

The aerodynamic method, also referred to as the "flux-gradient" method, was one of the two
techniques employed for estimating flux rates from the field treated with MON 119096 for this
field study given the available data. For the aerodynamic method, a mast was erected in the
middle of the treated field, and samples for air concentration measurement were collected at five

different heights, 0.15, 0.30, 0.55, 0.90, and 1.5 meters above the soil surface. Likewise, temperature and wind speed data were collected at 0.30, 0.55, 0.90, and 1.5 meters above the soil surface at a weather mast positioned just outside of the spray plot. Log-linear regressions were performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships were then utilized to calculate input parameters for the equation to estimate flux.

The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method in particular is the Thornthwaite-Holzman Equation, which is shown in the following expression:

$$\textit{Equation AD-1} \qquad P = \frac{k^2 (\Delta \bar{c})(\Delta \bar{u})}{\phi_m \phi_p [\ln\left(\frac{z_2}{z_1}\right)]^2}$$

where P is the flux in units of $\mu g/m^2 \cdot s$, k is the von Karman's constant (dimensionless ~0.4), $\Delta \bar{c}$ is the vertical gradient pesticide residue concentration in air (regressed) in units of $\mu g/m^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta \bar{u}$ is the vertical gradient wind speed (regressed) in units of m/s between heights z_{top} and z_{bottom}, and ϕ_m and ϕ_p are atmospheric momentum and vapor stability correction terms, respectively. The heights z_{top} and z_{bottom} are chosen to fall within the range of the sampler heights deployed in the field test, and, as indicated above, both the air concentration and wind speed values at these two heights are obtained from linear regression equations relating concentration and wind speed to the natural log of vertical height .

Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression are incorporated into Equation AD-1 to arrive at Equation AD-2 which is ultimately used to compute the flux.

$$\textit{Equation AD-2} \qquad Flux = \frac{-(0.42)^2 (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

ϕ_m and ϕ_p are internal boundary layer (IBL) stability correction terms determined according to the value of the Richardson number, R_i, which is calculated as shown in Equation AD-3:

$$\textit{Equation AD-3} \qquad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] * (u_{ztop} - u_{zbottom})^2}$$

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where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

Special Comments regarding EPA and Registrant's calculations for the flux estimation by the AD Method

Important special comments relating to the Registrant's use of the AD Method in the present submission are:

1. The original articulation of Equation AD-3 in this template document specified the denominator as the sum of the two bracketed terms, when in fact it should be specified as the product. This has been corrected in the text. The calculation in the EPA spreadsheet embedded with this document did correctly multiply the two terms.

2. While the equations above indicate that the exponent for calculating ϕ_m is -0.33 or +0.33 (depending on the value of Ri), the Excel spreadsheet for the aerodynamic method provided with this template uses the value +/- 0.30483 for this exponent. For the flux values provided by the Registrant in Table 5, the exponent value of +/- 0.33 has been used.

3. The flux values provided in Table 5 as Registrant values use 0.40 as the von Karman's constant (see, for example, Majewski, et. al., 1990) while the Aerodynamic Method calculations in the example spreadsheet use a value of 0.42.

4. The Registrant has corrected two cell assignment errors that are present in the example Excel spreadsheet for the aerodynamic method.

    i. In the Conc. Summary worksheet, the regression formulas in Columns I, J, and K, Row 3, reference the sampler heights specified by the User in Columns C through F, Row 2. However, the reference to the Row 2 Heights is lost when Row 3 of Columns I, J, and K, is copied down to other rows (sampling periods). This is because the reference to the Row 2 Heights is not specified as an absolute reference.

        Thus, as an example, the formula in Column J, Row 3 of the Conc. Summary worksheet should be "=INTERCEPT(C3:F3,LN(C$2:F$2))", wherein the addition of the "$" designation in the Row 2 references ensures that the reference to sampler heights always points to Row 2 when the formula is copied down to

subsequent sampling periods. This correction has been applied to Columns I, J, and K in the Conc. Summary worksheet.

    ii.   Similar referencing corrections have been applied to the wind and temperature regression formulas in Columns I, J, and K of the Met Data Summary worksheet to ensure that the appropriate row is specified when accessing the sampler height data.

5. The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid was not satisfied for the sampler positioned at 1.5 meter above the soil surface for any of the sampling times; however, the 0.90 meter value was used in the calculation. Also, flux and total mass loss values are in good agreement between the aerodynamic flux method and the Integrated Horizontal Flux Method. This agreement indicates that the fetch was of sufficient length for the aerodynamic method to be valid for this plot.

Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the "mass balance" method, was used as the second technique employed for estimating flux rates from the field treated with MON 119096 for this field study given the available data. For the integrated horizontal flux method, a mast was erected in the middle of the treated field, and samples for air concentration measurement were collected at five different heights, 0.15, 0.30, 0.55, 0.90, and 1.5 meters above the soil surface. Likewise, temperature and wind speed data were collected at 0.30, 0.55, 0.90, and 1.5 meters above the soil surface at a weather mast positioned just outside of the spray plot. A log-linear regression was performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log linear relationships for the atmospheric boundary layer. Subsequent wind speeds and air concentrations required as inputs to the equation used to estimate flux are then determined from these regression equations.

The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux (IHF) method in particular is given by the following expression:

$$\textit{Equation IHF-1} \qquad P = \frac{1}{x} \int_{Z_0}^{Z_p} \overline{c}\,\overline{u}\,dz$$

where P is the volatile flux in units of $\mu g/m^2 \cdot s$, $\overline{c}$ is the average pesticide residue concentration in units of $\mu g/m^3$ at height Z in units of meters, $\overline{u}$ is the average wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters for the sampling period in question, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top (the height at which air concentration falls to zero) in units of meters, and dz is the depth of an incremental layer in units of meters.

The text and the embedded spreadsheet that accompany this template document describe a numerical evaluation of the integral in Equation IHF-1 by application of the trapezoidal integration technique. In this case Equation IHF-1 is modified to the summation shown in Equation IHF-2, below (Yates, 1996):

$$\textit{Equation IHF-2} \qquad P = \frac{1}{x} \sum_{Z_0}^{Z_P} (A * Ln(z) + B) * (C * Ln(z) + D) dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), and z is the height above ground level. The embedded spreadsheet (and the Registrant) interprets Z_0 as the aerodynamic surface roughness, i.e., the point at which the wind speed profile extrapolates to zero velocity. In turn, the material supplied with this template document calculates Z_p, the height of the concentration plume, using Equation IHF-3, below.

$$\textit{Equation IHF-3} \qquad Z_P = \exp\left[\frac{(0.1 - D)}{C} \right]$$

However, the Registrant is not familiar with the derivation behind this equation for evaluating Z_p and uses instead the alternative (but similar) equations IHF-6 and IHF-7, as described in Comment 2 of the following Special Comments section.

Special Comments regarding EPA and Registrant's methods and calculations

Important special comments relating to the Registrant's use of the IHF Method in the present submission are:

1. The linear equations relating the wind speed and air concentration to the natural log of the height, Z, afford an analytical solution to the integral specified in Equation IHF-1. The Registrant utilizes this analytical solution to evaluate Equation IHF-1, rather than the numerical integration through application of the Trapazoidal Rule, represented in Equation IHF-2 and used in the provided embedded IHF spreadsheet.

   Thus, if

$$\textit{Equation IHF-4} \qquad P = \frac{1}{x} \int_{Z0}^{Zp} (C \ln(z) + D)(A \ln(z) + B) dz$$

   Then

   Equation IHF-5

$$P = \left[\frac{A \cdot C}{x}(z(\ln(z))^2 - 2z\ln(z) + 2z) + \frac{(A \cdot D + C \cdot B)}{x}(z\ln(z) - z) + \frac{(B \cdot D)}{x}z \right]_{Z0}^{Zp}$$

In which the symbols have the same meanings as those described for Equation IHF-2, above.

2. <u>Regarding Z$_p$, the upper limit of the indicated integration –</u>

The Registrant has not seen reference to an equation for calculating the height of the concentration plume that includes the subtraction of D from 0.1 in the numerator of the bracketed fraction seen in Equation IHF-3. Instead, the Registrant calculates the plume height as that value of Z at which the air concentration falls to zero. This is found by specifying a zero concentration in the regressed linear equation relating air concentration to the natural log of the height, Z, as seen in Equation IHF-6 below. Solving Equation IHF-6 for Z$_p$ yields Equation IHF-7. It is this value for Z$_p$ that the Registrant uses for the upper limit of the integral of Equation IHF-1. These Z$_p$ are also entered as Z$_{max}$ in the IHF Flux Analysis worksheet, Column N.

Equation IHF-6 $0 = C^* \ln(Z_P) + D$

Equation IHF-7 $Z_p = \exp\left[\frac{-D}{C}\right]$

3. <u>Regarding Z$_0$, the lower limit of the indicated integration –</u>

As specified in the example calculations provided with this template, the Registrant uses the Aerodynamic Surface Roughness, termed Z$_0$, as the lower limit for the integral of Equation IHF-1. Z$_0$ is the height at which the wind speed profile extrapolates to zero. In the present case this is found by specifying a zero wind speed in the regressed linear equation relating wind speed to the natural log of the height, Z, as seen in Equation IHF-8 below. Solving Equation IHF-8 for Z$_0$ yields Equation IHF-9. It is this value for Z$_0$ (for each sampling period) that the Registrant uses for the lower limit of the integral of Equation IHF-1. These Z$_0$ are also the values entered as the Aerodynamic Surface Roughness in the IHF Flux Analysis worksheet, column M.

Equation IHF-8 $0 = A^* \ln(Z_0) + B$

Equation IHF-9 $Z_0 = \exp\left[\frac{-B}{A}\right]$

4. As in the aerodynamic method spreadsheet, the regression equations in the Conc. Summary and the Met Data Summary worksheets contain non-absolute cell assignment

errors when referencing the user specified sampling heights. See Comment 4 in the Aerodynamic Method Section above. These errors have been corrected by specifying the sampling height references as absolute row addresses.

5. The minimum fetch requirement of 20 meters for this method to be valid was satisfied at all times. The treated field had an estimated slope of about 1%. The calculated maximum surface roughness was 0.025 m (Aerodynamic Surface Roughness in the IHF Flux Analysis worksheet, column M), which is below 0.1 meters, thus this method validity criterion was met.

6. <u>Regarding the value of x, the average fetch distance for a given sampling period</u> –

The Registrant and the example IHF spreadsheet embedded in this template document approach the calculation of x in slightly different manners.

For any given sampling period (Event), the Registrant calculates the average fetch by first calculating the wind speed weighted average wind angle over the course of the Event time window. This average velocity weighted wind angle is then used in a single calculation to calculate the average fetch. The embedded IHF spreadsheet, on the other hand, calculates average fetch by first calculating the fetch associated with the minute by minute wind angle data compiled in the Raw Met Data worksheet and then averages those results over the time period of the sampling event. In more concise terms, for each Event the Registrant calculates fetch from the wind speed weighted average of the raw wind direction data, while the embedded spreadsheet calculates fetch as the average of the raw fetch data.

The distinctions described above lead to minor differences in the fetch values used in IHF-5 when calculating flux by the IHF method.

B. Temporal Flux Profile

The flux as determined by the registrant as reported in MRID 49888503 and as determined by using the Excel spreadsheet provided by EPA in the Study Profile Template for the Field Volatility study (http://www.epa.gov/pesticide-registration/study-profile-templates#fate) for each sampling period after the application is provided in **Table 5**. Note that the Excel spreadsheet used for the flux calculation has been reviewed as described in Section A above to ensure that cell assignments are correct for each calculation.

Table 5. Field volatilization flux rates of MON 119096 obtained in Texas study, 0.5 lb a.e./A application rate

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			Notes
			EPA Spreadsheet ($\mu g/m^{-2}sec^{-1}$)	Registrant Report ($\mu g/m^{-2}sec^{-1}$)	Empirical Flux Determination Method	
1	06/08/15 13:40 – 20:22	6.7	0.000079 0.000200	0.000074 0.000197	AD IHF	
2	06/08/15 20:22 – 06/09/15 7:00	10.6	0.000013 0.000047	0.000011 0.000047	AD IHF	
3	06/09/15 7:00 – 20:00	13.0	0.000231 0.000282	0.000218 0.000277	AD IHF	
4	06/09/15 20:00 – 06/10/15 7:00	11.0	0.000036 0.000112	0.000031 0.000110	AD IHF	
5	06/10/15 7:00 – 20:00	13.0	0.000201 0.000209	0.000188 0.000226	AD IHF	
6	06/10/15 20:00 – 06/11/15 7:00	11.0	0.000021 0.000032	0.000019 0.000027	AD IHF	

Data obtained from Table 6, p. 40 and Tables 8-9, pp. 42-43 in the study report and the accompanying Excel spreadsheets.
*Methods legend: AD = Aerodynamic Method, IHF = Integrated Horizontal Flux.
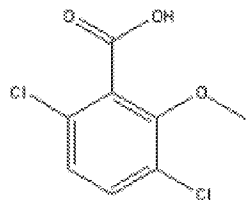
III. Study Deficiencies and Reviewer's Comments

1. The registrant uses a different approach to calculate Z_p, the top of the concentration plume, than that recommended by EPA when calculating volatilization flux rates using the Integrated Horizontal Flux method. This results in small differences between flux values calculated in the registrant report and in the accompanying EPA spreadsheets.

2. The decline of the test material was not clearly established. Sampling should be continued until the nature of the dissipation curve has been clearly established.

3. The minimum fetch required for use of the aerodynamic method was not satisfied for the sampler positioned at 1.5 meters above the soil surface.

4. Analytical method validation was performed, but the method was not independently validated. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.

5. The initial air monitoring period did not start at the beginning of the application period, but instead started immediately following the application period. The reviewer notes that off-field air samples were collected at a height of 0.15 m above the cotton canopy during the application period (6/8/2015; from 13:18 to 13:55) from eight locations around the test plot (5 m from the edge of the plot; p. 20; Table 6, p. 40; Figure 3, p. 47); however, the flux value was not reported because the study authors believed the calculated value was not representative of volatile flux because the samplers were placed in such a manner as to have potentially directly captured dicamba during the test application.

6. The test plot was not irrigated. The study design should include irrigation according to the label requirements.

7. Soil bulk density, soil temperature, soil moisture, and organic matter content were reported at only a single depth of 0-6 inches.

8. A control plot was not established.

IV. References

Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. Environmental Science and Technology, 24:1490-1497.

Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

Attachment 1: Chemical Names and Structures

Code Name/ Synonym	Chemical Name	Chemical Structure
PARENT		
MON 119096/ **Dicamba** **as the diglycolamine** **salt**	**IUPAC:** 3,6-Dichloro-*o*-anisic acid **CAS:** 3,6-Dichloro-2-methoxybenzoic acid **CAS No.:** 104040-79-1 **Formula:** $C_8H_6Cl_2O_3$ **MW:** 221.04 g/mol **SMILES String:** CLc1ccc(CL)c(OC)c1C(=O)(O)	

Attachment 2: Statistics Spreadsheets and Graphs

The electronic spreadsheet files are inserted below for calculations using the Aerodynamic Method and the Integrated Flux Method for determination of the emission rate of dicamba after application in the form of the diglycolamine salt in the formulation MON 119096.

1. Validation spreadsheet for studies following the Aerodynamic Method:

Field-volatility-835-8
100-MRID_49888503

2. Validation spreadsheet for studies following the Integrated Horizontal Flux Method:

Field-volatility-835-8
100-MRID_49888503

Attachment 3: Field Volatility Study Design and Plot Maps

Point	Latitude (°N)	Longitude (°W)
A	29.47796254	-95.99240953
B	29.47643949	-95.99135973
C	29.47733726	-95.98960948
D	29.47886396	-95.99066118
Flux Mast	29.47766695	-95.99102531
Wind Speed	29.47889961	-95.99065213
Weather Station	29.47886	-95.99062
Thermocouple Sensors	29.47886676	-95.99063166

Field Volatility Plot

Prevailing Wind

N

Sonic Anemometers

648 ft.

Thermocouple Stacks

A

D

Slope (1%)

Off-Field Sampling Locations →

Flux Sampling Mast

648 ft.

B

C
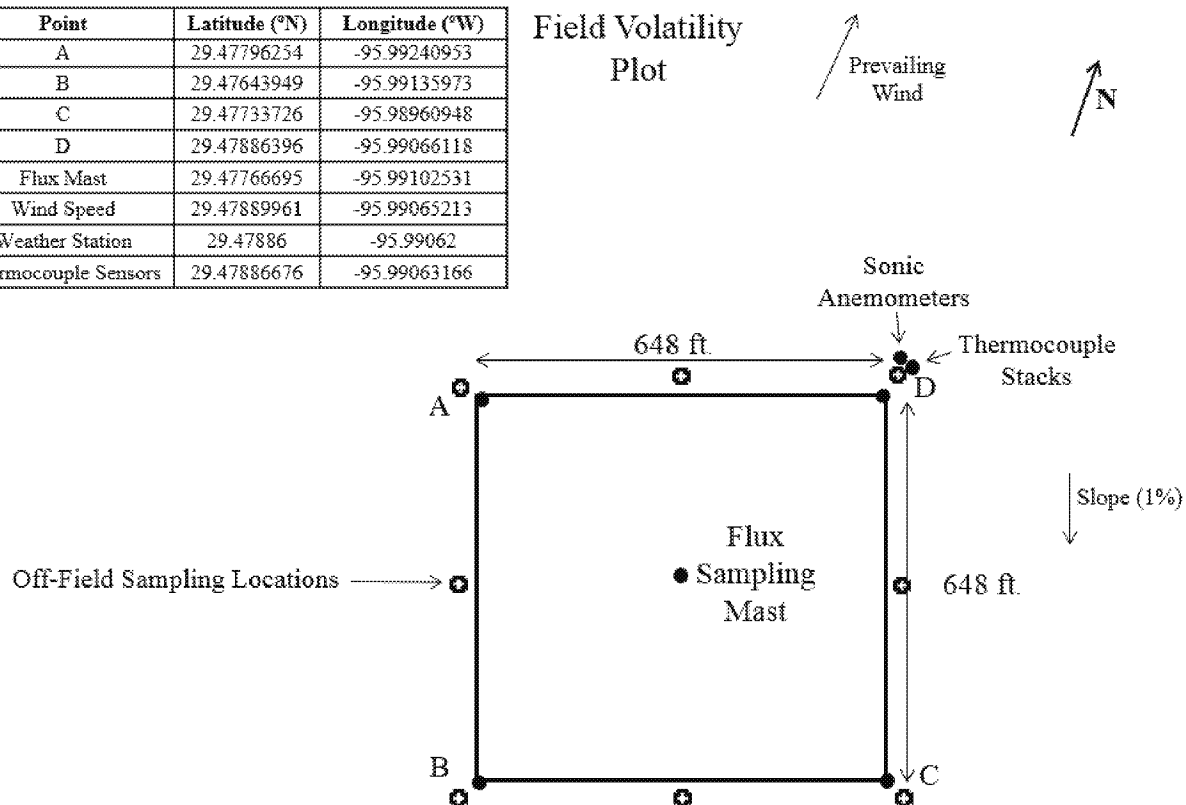
Figure obtained from Figure 3, p. 47, of the study report.

Attachment 4: Calculations and Index of Variables Used in Flux Determination Methods

Aerodynamic Method

$$\text{Equation } x_1 \qquad Flux = \frac{-(0.42)^2 (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\dfrac{z_{top}}{z_{bottom}}\right)^2}$$

Flux ($\mu g/m^2 s$): volatile flux of pesticide from release source surface

c_{ztop} ($\mu g/m^3$): concentration at the top sampler adjusted according to the regression of concentration vs. ln (height)

$c_{zbottom}$ ($\mu g/m^3$): concentration at the bottom sampler adjusted according to the regression of concentration vs. ln (height)

u_{ztop} (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

$u_{zbottom}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)

ϕ_m and ϕ_p (dimensionless): Internal Boundary Layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

$$\text{Equation } x_2 \qquad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\dfrac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] + (u_{ztop} - u_{zbottom})^2}$$

where:

T_{ztop}: Temperature at the top sampler adjusted according to the regression of temperature vs. ln (height)

$T_{zbottom}$: Temperature at the bottom sampler adjusted according to the regression of temperature vs. ln (height)

R_i (dimensionless): Richardson Number

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

Integrated Horizontal Flux Method

$$\text{Equation } x_3 \qquad P = \frac{1}{x} \sum_{Z_0}^{Z_P} (A * Ln(z) + B) * (C * Ln(z) + D) dz$$

P ($\mu g/m^2 s$): volatile flux of pesticide from release source surface
z (m): height above ground level
A (s^{-1}): slope of the wind speed regression line by ln(z)
B (m/s): intercept of the wind speed regression line by ln(z)
C ($\mu g/m^4$): slope of the concentration regression by ln(z)
D ($\mu g/m^3$): intercept of the concentration regression by ln(z)
Z_0 (m): aerodynamic surface roughness length of release source surface
Z_p (m): volatile plume top height; calculated from the following equation:

$$\text{Equation } x_4 \qquad Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$